Heavy metal pollution and coastal environmental change in South Australia: Evidence from carbonate sediments in the lower Coorong

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Abstract

This reconnaissance ICP-MS based study of the heavy metal composition of a core in proto-dolomites in a hyper-saline small lagoon in the lower Coorong reveals a distinctive record of geochemical change. A provisional interpretation of the core, estimated to cover a period of ~2-2.5 thousand years, has been made by inferences to the known chronology of industrial developments on the basis of metal signatures. The heavy metal signatures of nineteenth and twentieth century developments appear clear – for example – in distinctive peaks in the abundance of vanadium, chromium, copper, arsenic, and especially lead and uranium in the top 24 cm of the core, in particular fluctuations in the sources of emissions of lead that have existed – distant industrial sources, local vehicles and domestic sources, off-road recreational vehicles in the vicinity, perhaps power stations, as well as natural sources, may be apparent. A 'lead-focussed' approach may also suggest an earlier but less clear episode in the 19th century associated with the release of copper and arsenic that would reflect the known industrial history of the State. Changes in surface hydrology, re-working, chemical mobilisation and bioturbation are likely to have affected the concentrations of heavy metals deposited at the sediment surface. Distinctive longer term patterns of change are also indicated, on occasion with relatively sharp boundaries. These patterns and the changes between them were perhaps ultimately climatically-driven and modified in their record through complexes of biological, hydrological, geochemical and geomorphic processes. This study is unusual in that it has recovered a history of metal-cycling from an arid, coastal, calc-alkaline sedimentary arid environment. It broadens the range of environments from which to infer natural environmental and historical pollution histories.

Introduction

Metal pollution is not just a modern phenomenon. Neither is its legacy manifest only at its place of origin. For example, at the hemispheric scale, studies of the metal pollution burdens contained in retrieved ice-cores have indicated the metallurgical processes of the Ancient World of the Mediterranean have also left their mark in the form of distinctive and enhanced concentrations of lead and copper levels in the Greenland ice-core records (Hong et al. 1994, 1996 a & b; Rosman et al. 2000). Geochemical traces of human industrial activity, in addition to the consequences of 'normal' earth surface processes, have been extensively identified,

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predominantly in Europe. Often these studies are geochemical analyses of organic sediments which have been deposited in peat bogs and lake sediments (Dunlap et al. 1999; Farmer 1991; Mighall et al. 2002 a-d; Rosman et al. 2000; West et al. 1997). Useful geochemical histories of industrial pollution have recently been recovered from less promising environments, such as alkaline silts and sands that accumulated in a long-abandoned reservoir in the arid Jordanian desert (Pyatt et al. 1999; 2000). Analysis and interpretation of such geochemical records can allow quite detailed reconstruction of human activities, such as the mining and smelting of ores and their environmental responses over considerable periods of time (Gilbertson et al. 1997). Some studies have suggested that some environmental impacts may persist for millennia (Grattan et al 2003; Pyatt & Grattan 2001, 2002; Pyatt et al., 2002). Variations in trace metal concentrations from Australian coastal and lagoonal environments have distinguished 'modern' and perhaps 'contaminated' sediments from those of pre-industrial times and emphasised the importance of natural and anthropogenic metal sources (Preda and Cox 2002). Fluctuations in the heavy metal balance at a developing sediment surface, however, may also reflect natural events and processes that can vary over the shorter or longer terms as the input from natural sources and processes fluctuates (e.g. Hong et al. 1994, 1996 a & b; Matsumoto and Hinkley 2001; Pettke et al. 2000). However, even concentrations through lacustrine deposits of an element as widespread and mobile as arsenic (see Dembitsky and Rezanka 2003; Nriagu 1994; O'Neill, 1995) can be interpreted in historical-depositional terms (Spliefoff and Hemond 1996).

The site and study design

The study area is a small hyper-saline lagoon in the lower Coorong. South Australia, in general, and Coorong National Park in particular, have specific advantages for the study of past anthropogenic pollution. The study lagoon area is within the Coorong National Park and relatively well-described (Figure 1; & cf. Reeves and Gilbertson 1977). General studies of its history and natural history, with bibliographies of local research, were published by the Department of Environment and Planning (1988), Gilbertson (1981), Gilbertson and Foale (1977), National Parks and Wildlife Service (1996) and Noye (1974). This small lagoon is at the northern end of the Kingston lake chain described by Skinner (1963) and von der Borch (1976) and von der Borch and Lock (1979). To the north is the main lagoon of the Coorong. About 15-20 km to the north, and south of Salt Creek, there is a series of small and sometimes hyper-saline lagoons located east of the main lagoon. These distal ephemeral lakes (McFadden, Pellet Lake, Milne Lake, Halite Lagoon, Dolomite Lake, and North Stromatolite Lake) are frequently mentioned in relation to studies of the origins of dolomitic sediments that occur within them. These lagoons were estimated to have become separated from the sea about 6,500 years ago (see Gostin et al. 1988; von der Borch and Lock 1979), the resulting lagoonal facies eventually being replaced by an ephemeral lake facies. The importance of groundwater, surface hydrology, geochemical and biological processes, and bacterial activity in the formation of these Holocene dolomitic carbonate deposits has attracted much attention (see Gostin et al. 1988; Rosen et al. 1988, 1989; Tucker and Wright 1990;

and illustrated in von der Borch 1965; von der Borch and Lock 1979; West 1997; Wright 1999). Likewise, the living and late Quaternary lagoonal faunas and floras have received significant attention (Burne et al. 1980; Cann and De Dekker 1981). The introduction of magnesium and calcium ions through groundwater from sources in adjacent or underlying Quaternary aeolianites and volcanic bedrocks is a recurrent theme in the dolomite as a primary precipitate model (see von der Borch and Lock 1979). The rates of influx of other metals into them from groundwater, atmospheric fallout or overland flow do not appear to be known.

There is no definitive evidence of age at this particular study core site, but other lagoons in the present study are estimated to have become separated from the Southern Ocean to the west and the main Coorong Lagoon to the north over the last 2-2.5 thousand years (Harvey 1981); the result of intermittent sand drift, tectonic uplift, calcrete formation, and the processes of sand dune and lagoonal geomorphology. As occurs elsewhere in the study area, these lagoons appear to rest in shallow basins that are the cemented remains of basins in the former Pleistocene coastline, dominated by ridges of Pleistocene aeolianites and lagoonal infills that form a sequence that extends well back into the Quaternary and beyond (see Huntley et al. 1985; Schwebel 1984; Murray-Wallace and Belperio 1991; Murray-Wallace et al. 1991, 1999, 2001; von der Borch et al. 1980).

In the hot and dry summers, throughout the study area the lagoons dry-out completely. These resulting infill-deposits are often referred to locally as pipe-clays. These lagoonal deposits may be 'yoghurt-like' pelletal muds. As elsewhere in the area, they can form indurated muds, flake breccias, algal laminates, polygonal desiccation cracks and up-thrust tepee-like structures that over time may have disturbed any heavy metals deposited on surface sediments. Hilton (1976 a & b) noted that in places black algae can grow over the surface of the lake to produce a mat that can stabilise the dolomitic crust and prevent its loss by wind erosion in summer, and reported that the sediments accumulated at the rate of about 1mm per year. Depending upon particular circumstance at a site, heavy metals introduced by wind to the sediment surface might be protected and preserved essentially *in situ*, disrupted after deposition, and on occasion further re-worked by wind, water and living organisms.

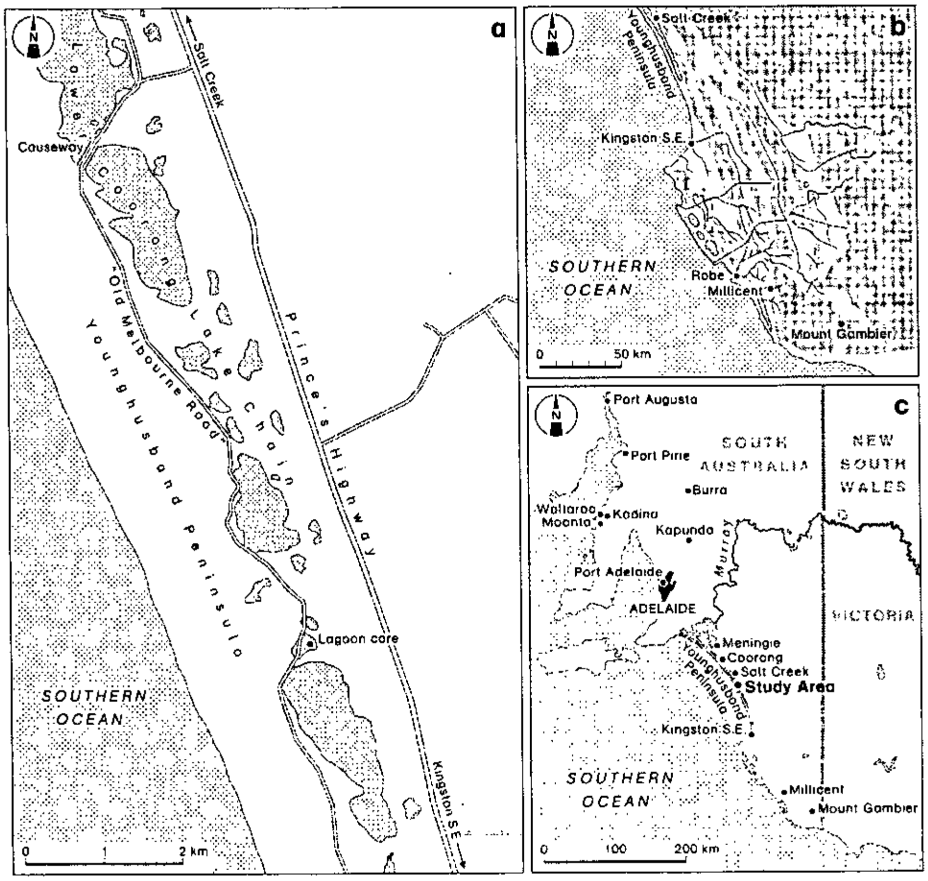
Whilst it is probable that the study deposits are late-Holocene in age, probably extending over 2-2.5 thousand years, the lagoon appears to be bounded in all directions by the low rises of carbonate sands of Pleistocene age that are cemented by calcrete soils (Brooke 2001). Calcrete-cemented sediments probably also underlie the lagoon. To the west are the vegetated or mobile carbonate sand dunes of Holocene age that form the modern Younghusband Peninsula. All these properties suggest that the white dolomitic sediments accumulating in the study lagoon may be, and have been in some part, insulated from any notable heavy metal contamination that might have been introduced by groundwater during the historic period. Sources of heavy metals undoubtedly exist in granitic bedrocks of the area, as well as in Pleistocene inter-dunal flats further inland, for example, where traces of iron, copper and cobalt have been detected (a & b). Until recently, any natural heavy metal load carried by surface freshwater inputs to these lagoons is likely to have declined substantially over the last one hundred years, as a result of the many surface drainage modifications from wetlands further inland described by Williams (1974) where there is significantly higher precipitation (see Gilbertson 1977, his Figure 4). As a result, much of these surface waters that used to enter the Coorong study area at Salt Creek no longer feed these lagoons, the water being diverted to flow directly to the sea much further to the south at Kingston and Millicent (Figure 1). Drainage at Salt Creek has, however, recently been modified to increase the flow of water back to the main Coorong lagoon.

Reconnaissance of the natural history of the area is given in reports in Gilbertson and Foale (1977). When full of water during windy and wet late Autumn to early Spring, aquatic grasses (*Ruppia*) and areas of blue-green algae are evident on the sediment surface of the study lagoon. At the margin of the lagoon are low-growing *Sarcocornia* (formerly referred to as *Salicornia*) with shrubby *Arthrocnemum*, and in places salt water tea tree (*Melaleuca halmaturorum*). The physical and biological limnology of this hyper-saline ephemeral lagoon is close to that of 'Point 4' of Geddes and Brock (1977). These data indicate that plants or animals that might cause substantial bioturbation of lagoonal sediments are distinctive and important but are relatively limited in numbers compared to other aquatic depositional environments. They may also interact with the geochemical processes associated with bacteria (Wright 1999). The alkaline geochemical environment is one in which the post-depositional vertical mobility of heavy metals is likely to be restricted in comparison with other more acid depositional settings.

Relevant climatic data are given in Gilbertson (1977). In that account, the wind climate is referenced to the work of Bourman (pers. comm.) as bimodal, the principal winds blowing from the southern or western quadrants; that is mainly from the vast expanses of the empty Southern Ocean. The resultant wind vector for winds greater than 16 km hr^{-1} at the lagoon calculated by Bourman is from the west, normal to the present shoreline. Winds from the north amount to approximately 10-15% of all winds.

Potential anthropogenic sources of pollutant metals in the 19th and 20th centuries in South Australia and Victoria which were likely to have produced metal pollutants are well understood. The study area is remote from major settlements and metal polluting industry and activities, and is rarely downwind of the present and former large sources of heavy metal pollution in South Australia or Victoria. Sources of lead in Metropolitan Adelaide are described in Gulson et al. (1995, 1996 and references therein) – these include domestic sources, vehicles, a variety of industries including a battery factory, a concrete plant, an oil refinery at Port Noarlunga and the coal-fired power station at Port Adelaide which is ~220 km to the north. The combustion of coal by power stations can release significant quantities of lead into the atmosphere. Copper extraction and minerals-processing between 1842 and 1923 in South Australia, that would also have yielded some lead, was located even further north in the Kapunda, Moonta, Kadina and Wallaroo districts (Figure 1). Flue

Figure 1 Location of the lagoon studied in the southern Coorong, South Australia (Tilley Swamp – 1:50,000 Topographic Map Sheet, 6825-II).



dusts from this minerals-processing is likely to have contained substantial quantities of arsenic as well as copper (O'Neill 1995). Further north again are the lead smelter at Port Pirie (Gulson et al. 1995, 1996 and therein), that commenced smelting ores from Broken Hill in 1899, and the coal-fired power stations of Port Augusta that were constructed in 1954 and 1960 (Figure 1).

The rural agricultural history of the study region area is given in Noye (1974), Paton (1977) and Williams (1974). It lacks any component that would have generated significant metal pollution – e.g. vehicle exhausts or pesticide use. Nevertheless metal pollution of the lagoon surface and the area must have taken place by airfall from vehicle emissions. Powered vehicles have probably been using the old Melbourne Road along the west margin of the study lagoon since the early decades of the twentieth century (Figure 1), but much vehicle use would have ended on this route following the construction of the new Princes Highway along the eastern margin of the study area. This route was started in the 1940s, the sealed road being officially opened in 1963. During this time, private vehicle numbers had begun a major and sustained increase in numbers. Unpublished motoring guides from the 1920s and 1930s describe driving and cycling conditions during summer on the exposed pipe-clay surfaces of the lagoons (Jack Victory, 1976; pers. comm.). From the early-mid 1970s, following relatively little activity in the 1960s, the surfaces of these pipe-clay lagoons and their environments were intensively used, when dry, by off-road recreational vehicles (ORRVs). In the study area, Welsh (1975) estimated that 500 people with ~100 ORRVs were driving on and around these lagoon surfaces, whilst Gilbertson (1981; 1983 his figs 19.4-19.6) estimated 230 vehicles hereabouts in the October long weekend of 1975. Numerous people have observed the erosional impacts caused by vehicles travelling on the lagoon surfaces and through their associated algal and halophytic vegetation (see Gilbertson 1981). It was the intensive and sustained use of off-road vehicles in this area that prompted the ORRV-impact and natural history surveys reported in Gilbertson and Foale (1977), and Gilbertson (1981, 1983). Field observations indicate that ORRV numbers on these lagoons and in the dunes subsequently declined rapidly with the introduction of ORRV access management in the 1980s in this National Park. Nowadays only local or tourist vehicle traffic passes along the coastal route, far larger traffic volumes proceed via the inland routes to Mount Gambier, Portland and Melbourne.

This general review suggests that in comparison with many other locations, the study site has many advantages for exploring pollution history over a period of ~2-2.5 thousand years. Much remains unknown. Not least is the absence of precise independent information on the age of these sediments, metal sources and pathways, and the significance of biological processes, secondary erosion and post-depositional disruptions of deposited heavy metals. Interpretations of evidence emerging from this reconnaissance clearly need to be cautious.

Methods

A 2 m deep core was obtained using a standard "Russian" corer. The observed stratigraphy is summarised in Table 1. Cores were stored in aluminium foil and analysed using the ICP-MS facility at the Institute of Geography and Earth Sciences, University of Wales Aberystwyth. These cores were analysed by Gareth Jones under the direction of John Gratton. Oven-dried 5 g samples were taken at 2 cm intervals down the core. These samples were digested for 72 hours in 10 ml of concentrated HNO_3. Ruthenium and blanks were used as standards for all analyses. After digestion, the samples were filtered through a #1 Whatman filter into 100 mL volumetric flasks. Subsequently, 2 mL of Ru (5 $\mu g\ mL^{-1}$) was added to each flask and then made up to 100 mL with Milli-Q water. Blank samples were also prepared at this time. Before sample analysis the blank sample was analysed (x3) followed by the 'all elems.' solution (x3). Each of the digested samples was then analysed (x1), and every 5-10 analyses were duplicated. At the end of each run (typically ~ 2 hours) a repeat analysis of the initial blank and 'all elems.' was performed to check for instrument drift. Raw data (in counts per second) were manipulated online, using the internal standard (Ru) within the samples, calibrated against Ru within the 'all elems.' standard. Data were now available in µg/g. Calibrated data were downloaded and the recorded blank was subtracted from each of the samples to give the actual trace metal content of

Table 1 Summary of the lithologies, and the concentrations of lead, copper, arsenic and strontium in Late Holocene sediments in the study lagoon.

Youngest

Lithology	Zone	Depth cm	Behaviour of lead, copper, arsenic & strontium	Character-istic
White "pipe clay"	1	0-10	Pb, progressive rapid increase from ~0 ug/g at 10 cm to peak of >~20 ug/g at 2 cm. Cu declines from ~1.7 to ~1 ug/g. As declines from 22 ug/g to 10 ug/g. Sr, rapid increase from ~2000 ug/g at 10 cm, to peak of ~3400 ug/g at 8 cm, and fall to ~2400 ug/g at 2 cm.	lead
	2	10-20	Pb, ~0 ug/g throughout. Cu oscillates – from ~0 to~2 ug/g. As oscillates - peak of ~10 ug/g, trough ~0 ug/g. Sr fluctuates between ~300 ug/g and ~3750 ug/g.	copper, arsenic
	3	20-26	Pb, rapid rise from ~1.5 ug/g to distinctive peak of ~9 ug/g at 22 cm then immediate fall to ~0 ug/g at 20cm. Cu declines from ~1.6 ug/g to ~0 ug/g. As oscillates from ~9 ug/g to ~3 ug/g. Sr fluctuates from ~1050 ug/g to peak of ~2100 pm at 24 cm and decline to 1050 ug/g at 20 cm.	lead, arsenic
	4	26-42	Pb, 0 to < 1ug/g. Cu slow overall decline from ~1.6 - ~1 ug/g. As oscillates between ~9 ug/g and ~2 ug/g. Sr, ~1250 ug/g at 42 cm, then rises to small peaks of ~1750 & ~2350 ug/g, then falls to 1050 at 20 cm.	copper
	5	42-50	Pb, fluctuations between 0 and <1 ug/g. Cu declines from 1.8 ug/g to 1.6 ug/g. As declines from ~15 ug/g to ~5 ug/g. Sr declines from ~3500 to ~1500 ug/g.	strontium, copper
	6	50-64	Pb, fluctuations between 0 and <1 ug/g. Cu declines from ~1.8 to ~1.3 ug/g. As peaks at 13-16 ug/g. Sr peaks of 4100 and 3400 ug/g.	arsenic, strontium

	7	64-84	Pb, fluctuations between 0 and <1 ug/g. Cu, three peaks; sustained and rapid rise to ~6.5 ug/g at 78 cm from 1.5 ug/g at 84 cm; subsequent smaller peaks 68 and 64 cm. As, oscillates between 6 and 15 ug/g, with peak over 27 ug/g at 80 cm. Sr, ~1500-~2400 ug/g, with highest peak over 4400 ug/g at 78 cm.	copper, arsenic, strontium
	8	84-126	Pb, minor fluctuations between ~1 and ~2 ug/g. Cu minor oscillations between ~2-2.5 ug/g. As consistent rise from ~2 to ~10 ug/g. Sr, varies systematically between ~2200 and ~3100 ug/g, low value of ~750ug/g at 112 cm.	strontium, lead
	9	126-225	Pb. varies between ~0.5 and ~2 ug/g. Cu varies between 2-2.8 ug/g, minor oscillations, single isolated peak of ~5 ug/g at 192 cm. As typically between ~2 and ~3 ug/g, single isolated peak of ~6 ug/g at 192 cm. Sr, systematic increase from ~500 ug/g at 220 cm to ~2750 ug/g at 120 cm; isolated peak concentration of ~3700 ug/g at 194 cm.	strontium
Green – muds	10	225-242	Pb, ~4-5 ug/g at 242 cm declining to ~1 ug/g at 225 cm. Cu, oscillating overall decline from 242 to 225 cm. As sustained decline from 15 ug/g at 242 cm to 1.5 ug/g. Sr, fluctuates between ~500 and ~1000 ug/g.	lead, copper, arsenic

Oldest

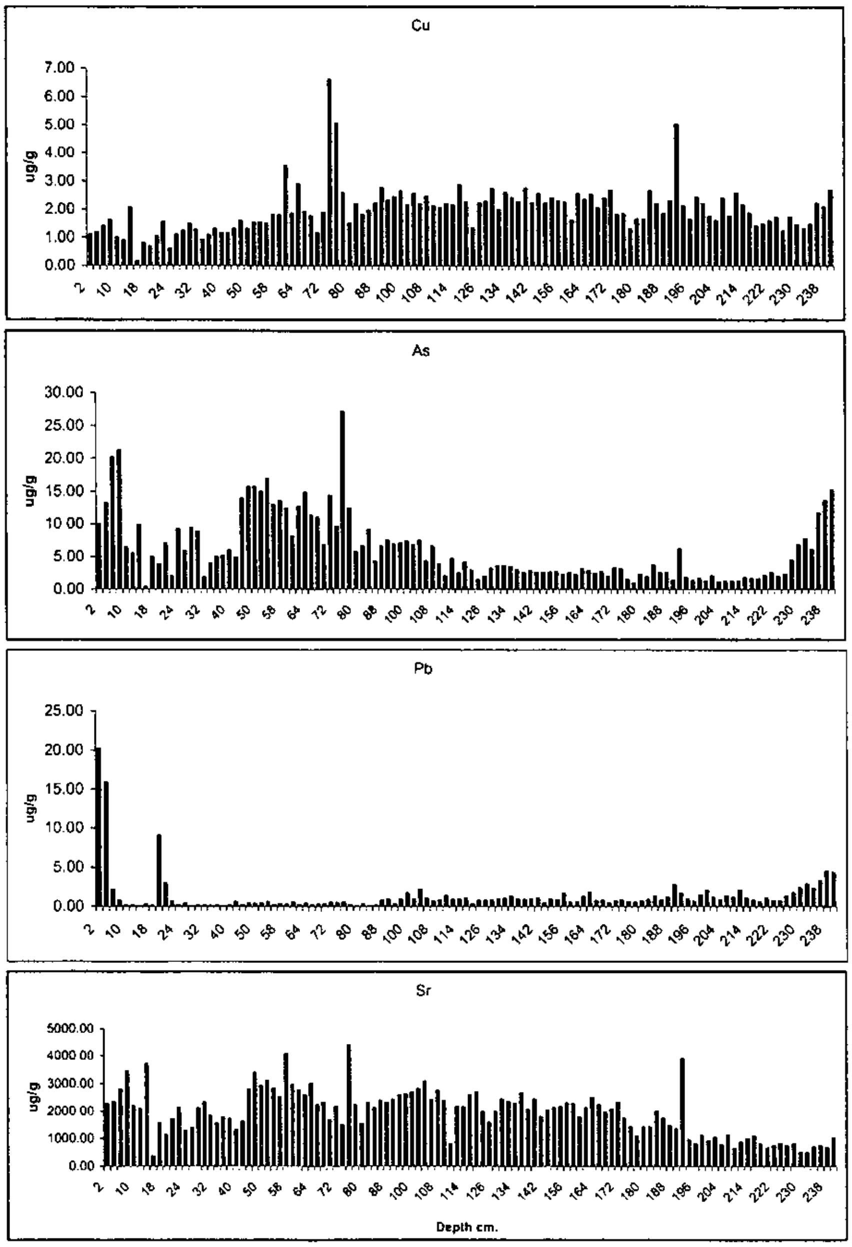
each soil sample in µg/g.

The present study focuses upon the concentrations of lead, copper, arsenic and strontium, with minimal attention to concentrations of vanadium, chromium and uranium (Figure 2; Table 1), although this particular ICP-MS study provided information on a total of thirty-eight isotopes. All these elements play important parts in the modern world, for example in industrial and metallurgical processes, domestic life, transport, in materials, or in fossil fuels. In particular, lead might reflect airborne pollution from vehicle emissions, minerals processing and power generation, as well as long-distance sources such as Port Pirie. Copper and arsenic might reflect the regional impact of historical minerals processing in South Australia. Strontium is reported because it substitutes to differing degrees for Ca^{2+} and Mg^{2+} in the dolomite mineral lattice. Hence it serves as a surrogate for the presence of dolomitic sediment.

Description and interpretation

The stratigraphy of the lagoon core is

Figure 2. The abundance in ppm of lead, copper, arsenic and strontium from a core through the pipe-clay in a small lagoon in the southern Coorong, South Australia.



summarised in Table 1. This differs slightly from the four-fold lithological division of deposits noted in the distal 1989; von der Borch and Lock 1979). In the present study area near-shore marine or large lagoonal environment are also represented at the base of the core. They are replaced at about 225 cm depth by white pelletal muds – pipe-clays – that characterise the modern, ephemeral, and hyper-saline lagoon. In the core samples no further lithological change could be detected. Neither was visible evidence of any other significant stratigraphic break in the sediment core detected. Reference to the geomorphological work of Harvey (1981) suggests that the change from marine to pipe-clay deposits at about 225 cm depth took place 2-2.5 thousand years ago. Sediment in this lagoon therefore appears to be accumulating at broadly the same rate as that reported by Hilton (1976, a & b), approximately 1 mm per year.

Cursory inspection of the metal concentration data in Figure 2 indicate that they display distinctive patterns – in terms of abundance, composition, parallelism of trends and episodes of change or transition. There is therefore a palaeoenvironmental story to be derived from them. To assist interpretation of these quantitative metal concentration data, these lagoonal sediments have been divided into eight 'metal-assemblage zones' that are shown in Table 1 and Figure 2, following the approach of Pyatt et al. (1995) that focuses upon both concentrations and trends of key metals.

Heavy metals

The data shown in Table 1 and Figure 2 indicate that substantive variations in heavy metal concentrations are present. ephemeral lakes east of the Coorong lagoon and south of Salt Creek by von der Borch (1976; Rosen et al. 1988; In four cases, clear patterns are evident in the data. At a very general level, explanation – albeit of a general kind – appears relatively straight-forward.

1. The relatively metal-rich, lowest body of sediment between 242-225 cm depth noted as Zone 10 corresponds with sediments in the field that were recognisably marine. The gradual reduction through Zone 10 of concentrations of metals that are naturally present in ocean water – copper, lead, arsenic – suggests a transition from a marine environment to that resembling the present day, rather than a sharp single event that might be inferred from the borehole evidence. Strontium is of course also abundant in ocean and other waters as well as in the lithosphere and biosphere. When seen in terms of the sediment lithology, the increasing concentrations of strontium in this core appears to reflect the development in the lagoon of the type of dolomitic carbonate sediments reported by von der Borch (1976) and von der Borch and Lock (1979).

2. The progressive increases in the concentrations of strontium upwards from 225-230 cm through the core to core depths of 42 cm through zones 9 to 5 suggest the progressive dominance of the deposition of carbonate muds – the white pipe clays – in a lagoon that had become isolated from the waters of the Southern Ocean by the progressive development of the coastal barrier immediately to the west of the Younghusband Peninsula (Figure 1). This evidence suggests that this small lagoon had broadly adopted the characteristics of the present environment. Extrapolation of the 1 mm

surface growth rate model suggests these deposits accumulated in the period from about ~2,200 to ~400 years ago. The abundance of lead, copper and arsenic probably reflect input of metals directly to the lagoon as long distance dust, from oceanic sources as precipitation and spray, from elements brought to the lake in surface waters via Salt Creek from further inland (Figure 1) and introduced in ground water – the overall composition reflecting bedrock, biological, terrestrial, oceanic and atmospheric sources. Concentrations of lead reach very low levels at about 90 cm. The notable change in concentrations of strontium, arsenic and copper occur at about 50 cm. This may have a number of causes. It might, for example, indicate an unrecognised erosional hiatus. The copper peak at 78 cm appears anomalous. At present it is regarded as a naturally occurring unusual fluctuation. In contrast to units 9 – 6, however, the deposits in zones 4 and 5, 26-50 cm, have very low concentrations of heavy metals – a property shared by the deposits of zone 2 between 10 - 20 cm. These are discussed further below.

3. The notable peak in lead that defines Zone 3 from 26-20 cm depth. This is accompanied by a parallel changes in the abundance of arsenic, and in a more subdued form, of copper. Concentrations of strontium decline. It is tempting to identify this peak as, in some part, a long distance result of metalliferous mining and smelting further north between 1842 and 1923 described by Heathcote (1994). Pollution might have stemmed from several stages in minerals processing: mining and extraction, ore crushing and grinding, smelting, and transport. Lead concentrations are however relatively low throughout this body sediment. The mining and smelting of lead ores in the Adelaide Hills and Ediacara in South Australia at this inferred time was comparatively limited in scale. Lead as well as copper and other metals were liberated into the atmosphere from the fuel used during copper ore processing further north. Burra, for example, 160 km north of Adelaide (Figure 1), became one of the largest producers of copper ore in the world.

Studies of atmospheric aerosol pollution plumes from metropolitan Adelaide, the Port Noarlunga oil refinery, the Port Pirie lead smelter and Port Augusta power station are all shown on satellite imagery extending 170-250 km kilometres downwind by the NASA TRRM satellite (NASA TRRM and http://daac.gsfc.nasa.gov/CAMPAIGN_DOCS/hydrology/hd_trmm_intro.html), and are illustrated and reported in a different context by Rosenfeld (1999). As a result it is likely that northerly winds could transport small quantities of copper, lead and other heavy metals in gases and aerosols from sources areas further north to the study lagoon.

4. The concentrations of lead in Zone 1 – the upper 10 cm of the core – are ten to twenty times higher than in other lagoonal pipe-clay deposits. Given the observed number and intensity of vehicles driving off-road on these surfaces in the 1970s and early 1980s (Gilbertson 1981, 1984, Walsh 1975) it seems likely that the lead-rich nature of the uppermost 0-4 cm of the deposits reflects this very local use of lead-enriched fuels, as well as by nearby vehicles on the adjacent old and new Princes Highway. Lead-enriched petrol was introduced in the United States in 1923 and it is known that lead aerosols can be transported long distances in the atmosphere, although most lead pollution from vehicles is deposited within 15 m of the 'road' (Alloway

1995). Longer distance sources from large domestic, industrial and power generating sites further north, as well as from other more local sources, may have also contributed to these uppermost deposits, but at present it is difficult to distinguish them. These uppermost deposits mark the end of a dramatic increase in lead concentration that begins at a depth of 10 cm. Extrapolation of a 1 mm per year increase over 10 cm represents (very generally) perhaps one hundred years, indicating this lead trend may provide one local reflection of the more general changes in South Australia. Williams (1974) shows that the numbers of petrol-diesel vehicles in use in the State was in the order of 40-50,000 in the 1930s and 1940s – a figure that had increased seven-fold by 1970 – and that population increases in Adelaide and the State, more generally, also display broadly similar trends. As a result it seems likely that the pattern of lead increase between 10 and 4 cm was also mainly caused by other more generalised sources of lead emissions.

Details and problems of interpretation

These provisional interpretations have re-emphasised the need to explore in the study area the following lines of evidence that underpin them:

- the antiquity of the transition from marine to lagoonal conditions,
- extrapolation back over time of an observed rate of sediment surface growth;
- inferences on the role of strontium;
- assumptions on the sources and pathways of copper, arsenic and lead;
- a restricted role for bioturbation, metal mobility and sediment stability, and:
- in the upper part of the core, that inferred patterns of lead increase can be related to regional and local events in the 19th and 20th centuries;
- it is the element lead rather than copper that offers the best clue to the wider human history of 19th and 20th century at the site.

Several other features merit further consideration in the geochemical data. Sudden decreases and increases in concentrations in the core, for example, might reflect unseen hiatuses in the core. They might reflect erosional and/or depositional changes, as much as changes in the rate of input of metals. Such explanations remain to be examined. We have no evidence that they correspond with changes in texture, organic or other property of the sediment. The evident sharpness of such boundaries suggests the vertical movement of metals through bioturbation or physico-chemical processes have been of limited effect.

It is possible that the impact of drainage diversion at Salt Creek in the area may also have played a key role in the heavy metal budget of the study lagoon (Figure 1). This effect of drainage in the swamps and pools inland began in the 1870s, but is most likely to have impacted upon Salt Creek waters from about 1881-1899 (Williams 1974, p. 181) and may have brought about a lowering in the input rate of lead and copper in surface waters. Secondary effects would be that the accreting sediment surfaces, with their metal burden, and floras of halophytes, algae and bacteria, may have been exposed to enhanced rates of erosion and deposition, perhaps accelerating the re-cycling of pre-existing pipe-clays. Greater desiccation of the lagoon surface may also have affected the extent to which heavy metals ultimately may become incorporated into surface sediments through the activity of macrophytes, and surface algae and bacteria. Such changes may be the cause of the low concentrations of heavy metals in zone 2, between 10-20 cm; a time when the present interpretation suggests concentrations of heavy metals from domestic, industrial, power-generation, and mining operations were anticipated to be increasing the overall environmental heavy metal burdens.

Between 222 and 50 cm there are interesting, quasi-parallel and sometimes inverse relationships between the concentrations of lead, arsenic and copper. At 90 cm, the steady low concentrations of lead decline to similarly steady much lower concentrations whilst arsenic concentrations begin a sustained increase and copper concentrations exhibit a more patchy but overall parallel slow decline. Much remains obscure, for example, the trends in arsenic appear significant and suggest they might be interpreted in terms of a changing depositional environment, rather than as the consequences of post-depositional mobility.

At present there are several possible explanations of these various features. On the basis of present information, it seems likely that deposits below ~30 cm predate any of the European influences mentioned above. Changes in the geochemistry below these levels therefore may stem from a number of causes – singly or more likely in combination. Although aboriginal activity and natural burning took place in the adjacent sand dunes of the Younghusband Peninsula (Gilbertson 1981; Leubbers 1978; Tindale 1938), no evidence of significant impact, such as charcoal, for example, has been detected in this particular core. Local or regional scale environmental fluctuations are also likely to have had a notable influence. The 'Little Ice Age' (LIA) of the period from ~1450 to 1850 AD, recognised widely in the northern hemisphere, also appears to be evidenced in New Zealand (D'Arrigo et al. 1998; Purdie and Fitzharris 1999; Wilson et al. 1979; Williams et al. 1999; Winkler 2000) and Tasmania (LaMarche and Pittock 1982). These climatic fluctuations are likely to have some manifestation in the climatically exposed study area, whether or not the LIA was a truly global phenomenon. This episode appears to have been preceded by a time of slightly different climate. If this is correct, then the study site is likely to have experienced both increases and decreases in prevailing temperature, precipitation, water balance, storminess and wind climate. These in turn would have influenced biological activity, and biological and chemical decay processes, as well as groundwater regimes. Since the oceans, bedrocks and surficial deposits and the biosphere are also substantial reservoirs of the study elements, the patterns of trends and 'breaks' displayed in zones 9 through to 4 at the lagoon site might represent an amalgam of distinctive climatically-driven events. Overall, this new evidence does not indicate the need to find explanations of these trends in metals in events that lie outside the present State and its adjacent seas.

Conclusions

This reconnaissance ICP-MS based study of the heavy metal composition of a core in proto-dolomites in a hyper-saline small lagoon in the lower Coorong has demonstrated a distinctive record of geochemical change – pointing to the future utility of this type of approach. A provisional interpretation of the core has been estimated by extrapolation from elsewhere – on the basis of rates of sedimentation and the longer term history of geomorphic change to cover a period of ~2-2.5 thousand years. This has provided a tentative chronology of the events on the basis of metal signatures.

The heavy metal signatures of nineteenth and twentieth century developments in the State may be clear. Within this inferred historic period, more detailed analysis of distinctive changes that are evidenced is prevented by present uncertainties on the dating, natural and artificial sources and the pathways of these metals, in particular for copper and arsenic. Nevertheless, interpretation based upon the abundance of lead, together with vanadium and uranium, in the core suggests this last phase of deposition took place the late 19^{th} and through the 20^{th} century, and records fluctuations in sources of emissions of lead that have existed – distant industrial sources, local vehicles and domestic sources, Off-Road Recreational Vehicles in the vicinity, perhaps power stations, as well as natural sources. A 'lead-focussed' approach may also suggest an earlier but less clear episode in the 19^{th} century associated with the release of copper and arsenic, that would reflect the known industrial history of the State. Changes in surface hydrology, re-working, chemical mobilisation and bioturbation are likely to have affected the concentrations of heavy metals deposited at the sediment surface. Distinctive longer term patterns of change are also indicated, on occasion with relatively sharp boundaries. These patterns and the changes between them were perhaps ultimately climatically-driven and modified in their record through complexes of biological, hydrological, geochemical and geomorphic processes that merit further investigation. At present there are no reasons to suspect that the trends detected here reflect events outside the present Sate of South Australia. This study is unusual in that it has recovered a history of metal-cycling from an arid, coastal, calc-alkaline sedimentary arid environment. It broadens the range of environments from which to infer natural environmental and historical pollution histories.

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